THE FREE ENERGY OF DILUTION OF ACTIVITIES OF THE IONS OF POTASSIUM BROMIDE IN AQUEOUS SOLUTIONS

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HARRY BRYANT HART

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE COLLEGE OF THE STATE UNIVERSITY OF IOWA
1921

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THE FREE ENERGY OF DILUTION AND THE ACTIVITIES OF THE IONS OF POTASSIUM BROMIDE IN AQUEOUS SOLUTIONS.

In a study of "The Activity of the Ions and the Degree of Dissociation of Strong Electrolytes," Lewis[1] has calculated the degrees of dissociation of a large number of uni-univalent salts. These calculations are based on the assumption that in solutions of different electrolytes containing a common ion this ion has the same mobility at any one concentration. From the results obtained he finds that in a 0.1 *M* solution the chlorides, bromides and iodides of hydrogen and the alkali metals are all dissociated to practically the same extent. In order to interpret the changes in the transport numbers of the ions which accompany change in concentration he advances two hypotheses: "(1) that all the ions increase in mobility with increasing ion concentration, the increase being relatively greater, the greater the original mobility; (2) that all the ions decrease in mobility with increasing ion concentration, the decrease being greater the smaller the original mobility." He concludes that the first of these hypotheses is the more probable and advances two probable causes for an increase in ionic mobility with increasing concentration. These are: (1) a gradual

[1] Lewis, *J. Am. Chem. Soc.*, **34**, 1631 (1921).

dehydration, which although undoubtedly present does not play a dominant part, and (2) an added increase in the ordinary conductivity of the electrolyte due to a conduction of the Grotthus type. The additional conduction due to this effect would account for the assumed increase in mobility.

Making the same assumption regarding the independent mobility of the ions, MacInnes[2] also finds that the alkali chlorides are dissociated to the same extent in 0.01 *M* concentration. This observation led him to advance the hypothesis that for the same molal concentration the activity of the chloride ion is a constant and is independent of the cation associated with it. Further on the basis of the striking similarity of the weight and the mobility of the potassium and chloride ions he assumes that these ions have the same activity in a solution of the salt. Using the available electromotive-force data, MacInnes has calculated the activities of the ions in various solutions of potassium chloride and hydrochloric acid.

Noyes and MacInnes[3] have calculated for a wide range of concentrations the mean activity coefficients of the ions of potassium chloride, hydrogen chloride, lithium chloride and potassium hydroxide.

During recent years there has developed the hypothesis of complete dissociation of strong uni-univalent electrolytes. The possibility of complete dissociation was first suggested by Noyes,[4] and the hypothesis has been further substantiated by the work of Milner,[5] Ghosh,[6] Bjerrum,[7] Brönsted,[8] Hill[9] and others. While this hypothesis demands that the electrolyte be completely dissociated at all concentrations, the number of ions actually free at any one time is limited by various factors involved in the solution process. For any given concentration of the electrolyte a definite fraction of the ions are loosely united, as a result of electrostatic attraction, to such an extent that they are not capable of independent activity and mobility. These "bound" ions, therefore, possess the properties which we have usually attributed to undissociated molecules. Hence, there should exist in a solution of an electrolyte an equilibrium between the electrically bound ions and the simple ions which in the "free" state are capable of independent activity and mobility.

In a recent paper Harned[10] has found that the hypothesis of complete

[2] MacInnes, *J. Am. Chem. Soc.*, **41**, 1086 (1919).
[3] Noyes and MacInnes, *ibid.*, **42**, 239 (1920).
[4] Noyes, *Int. Congress Arts Sci.*, St. Louis, **4**, 319 (1904).
[5] Milner, *Phil. Mag.*, [6] **23**, 551 (1912); **25**, 753 (1913); **35**, 352 (1918).
[6] Ghosh, *J. Chem. Soc.*, **113**, 449, 627, 707 (1918).
[7] Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918); *Z. anorg. Chem.*, **109**, 275 (1920).
[8] Brönsted, *J. Am. Chem. Soc.*, **42**, 761 (1920).
[9] Hill, *ibid.*, **43**, 254 (1921).
[10] Harned, *ibid.*, **42**, 1808 (1920).

dissociation is a good working hypothesis. He has also confirmed the MacInnes hypothesis of the independent activity of the ions. Furthermore, he has computed the individual activity coefficients of the hydrogen, sodium, potassium, lithium and chloride ions in concentrations 0.1 to 3.0 *M*.

Up to this time practically all of the work dealing with ionic activities has been confined to a study of the ions in aqueous solutions of the alkali chlorides and hydrochloric acid. We have thought it worth while, therefore, to extend these investigations by a study of the activity of the ions in solutions of potassium bromide, thus making possible a direct comparison of the activities of the chloride and bromide ions.

Materials and Apparatus.

Potassium bromide of a high grade was further purified by crystallizing twice from distilled water and twice from "conductivity" water. The mercury used in preparing the amalgam was first repeatedly sprayed through a long column of dil. nitric acid and then distilled in a current of air under reduced pressure.

In preparing the silver bromide electrodes small pieces of platinum foil, in the form of electrodes, were first electrolytically plated with a firm white deposit of metallic silver. They were then arranged as anodes in a solution of potassium bromide and coated with silver bromide, using a current density of 2 m. a. for 15 minutes. The electrodes thus prepared are of a steel-gray color and are easily reproducible to within 0.05 m.v. The potassium amalgam was made by distilling mercury over into metallic potassium, *in vacuo*, after the method of Lewis and Kraus.[11] It was then filtered through a fine capillary into a suitable storage flask and preserved under an atmosphere of pure dry hydrogen. The amalgam used throughout contained 0.2122% of metallic potassium.

Owing to the fact that the oxidation of the potassium by dissolved oxygen materially changes the potential of the amalgam electrodes, every possible precaution was taken to exclude air from the solutions. To this end the exact amount of salt for a given volume concentration was transferred to a volumetric flask fitted with a stopper and a filling device permitting easy transfer of the solution to and from the flask. Water was then added and the solution boiled. To insure the removal of every trace of air a stream of pure hydrogen was bubbled through the boiling solution. The solution was then cooled to the desired temperature and diluted to the desired volume by adding conductivity water which had been similarly treated. The solution was then weighed on a sensitive balance and its molal concentration calculated. At no time thereafter nor during the potential measurements which followed did the solution come into contact with the air.

A large oil-bath electrically controlled gave temperatures constant to 0.02° for any desired temperature. All potential measurements were made on a Wolff potentiometer, using as a standard of reference a recently certified Weston cadmium cell, (No. 3554: 1.01956 volt).

Precision and Duplication.

Three silver bromide electrodes having a maximum variation of not more than 0.05 m.v. were placed in each half-cell and allowed to stand until equilibrium was established between the electrodes and the potassium bromide solution. A period of 4 hours was found to be sufficient for this purpose. Only those electrodes in any half-cell were

[11] Lewis and Kraus, *J. Am. Chem. Soc.*, **32**, 1459 (1910).

used in the measurements which checked, over all, to 0.03 m.v. In case no such agreement was attained the cell was dismantled and set up anew. When at any temperature the electromotive forces had become constant final readings were taken and the temperature changed. In this way the electromotive forces of the various cells were obtained at 25°, 30° and 35°.

Experimental.

In the present work the following types of cells have been studied: (A) Ag | AgBr, KBr (c) | K.Hg$_x$; (B) Ag | AgBr, KBr (c_1) | K.Hg$_x$—Kg$_x$.K | KBr (c_2), AgBr | Ag; (C) Hg$_x$.K | KBr (c_1), AgBr | Ag—Ag | AgBr, KBr (c_2) | K.Hg$_x$; (D) Ag | AgBr, KBr (c_1) | KBr (c_2), AgBr | Ag; (E) Hg$_x$.K | KBr (c_1) | KBr (c_2) | K.Hg$_x$.

Measurements of the Cells.—The amalgam electrodes employed are similar to those first used by Lewis and Kraus,[11] and later by Allmand and Polack.[12] The mean value of the electromotive forces for at least two successive set-ups of this type of cell for any one concentration are given in Table I. The values of the electromotive forces for these different set-ups do not differ by more than 0.10 m.v., except for the 2.8032 M concentration where a difference of 0.20 m.v. was observed. The values of the electromotive forces of a cell containing exactly 0.10 M concentration of potassium bromide at the three temperatures was calculated by means of an empirical quadratic equation expressing the electromotive force as a function of the concentration. These values are inserted at the bottom of Table I. The electromotive forces for the 0.25258 M, 0.10048 M and 0.050148 M were used in these calculations.

TABLE I.

ELECTROMOTIVE FORCES OF THE CELLS.

(A). Ag | AgBr, KBr (c) | K.Hg$_x$.

Moles per 1000 cc.	Moles per 1000 g. H_2O.	E_{25} volts.	E_{30} volts.	E_{35} volts.
2.5000	2.8032	2.0235	2.0089	1.9948
1.0000	1.03486	2.0792	2.0657	2.0518
0.5000	0.51048	2.1108	2.0976	2.0849
0.2500	0.25258	2.1432	2.1308	2.1179
0.1000	0.10048	2.1858	2.1740	2.1624
0.0500	0.050184	2.2183	2.2071	2.1958
0.0100	0.010021	2.2948	2.2848	2.2753
0.0050	0.0050096	2.3289	2.2196	2.3098
0.0010	0.0010017	2.4081	2.4002	2.3927
	0.1000	2.1861	2.1743	2.1627

The Free-energy Decrease and the Heat-content Decrease Attending the Cell Reaction.—The free-energy decrease ($-\Delta F$), expressed in joules, attending the reaction in any cell is obtained by multiplying the electro-

[12] Allmand and Polack, *J. Chem. Soc.*, **115**, 1020 (1919).

motive force of the cell by 96494. If now we express the free energy decrease as a function of the temperature by means of the equation,

$$(-\Delta F)_t = (-\Delta F)_{25}\,[1 + \alpha(t-25) + \beta(t-25)^2],$$

we can calculate the temperature coefficients of free energy decrease. These values together with the free energy decrease are collected in Table II. The values for the decrease in heat content $(-\Delta H)$ attending the cell reaction given in the same table have been calculated with the aid of the thermodynamically derived relation,

$$(-\Delta H)_{25} = (-\Delta F)_{25}[1 - \alpha \times 298.09].$$

TABLE II.

THE FREE-ENERGY DECREASE AND THE HEAT-CONTENT DECREASE ACCOMPANYING THE CELL REACTION.

c.	$(-\Delta F)_{25}$ joules.	$(-\Delta F)_{30}$ joules.	$(-\Delta F)_{35}$ joules.	$\alpha \times 10^6$.	$\beta \times 10^6$.	$(-\Delta H)_{25}$ joules.
2.8032	195256	193846	192447	−1448.0	+1.0	279527
1.03486	200630	199328	197985	−1279.0	+3.8	277130
0.51048	203679	202396	201180	−1274.0	+4.7	281036
0.25258	206825	205609	204365	−1133.4	−4.7	276711
0.10048	210916	209778	208659	−1087.5	+1.7	279296
0.050184	214072	212971	211827	− 995.7	−2.8	277609
0.010021	221463	220469	219552	− 893.0	+4.3	280416
0.005009	224753	223822	222881	− 776.0	−4.4	276760
0.001001	232416	231604	230883	− 672.5	+3.3	279015
0.10000	210945	209807	208688	−1088.0	+1.6	279355

Although of the same order of magnitude the values of $(-\Delta H)$ are irregular. These irregularities are, however, within the limits of experimental error. The effects due to a simultaneous error of 0.10 m.v. at 25° and 35°, respectively, have been calculated. While a deviation of this magnitude causes a variation of only 0.005% in the value of $(-\Delta F)$ it produces a change in the temperature coefficient (α) sufficient to produce an error of 2% in the value of the heat-content decrease.

The Free-energy Decrease Accompanying the Transfer of One Mole of Potassium Bromide from Various Concentrations (c) to 0.10 M.—

TABLE III.

THE FREE-ENERGY DECREASE ATTENDING THE TRANSFER OF ONE MOLE OF POTASSIUM BROMIDE FROM CONCENTRATION (c) TO 0.10 M.

c.	$(-\Delta F)_{25}$ joules.	$(-\Delta F)_{30}$ joules.	$(-\Delta F)_{35}$ joules.
2.8032	15689	15961	16241
1.03486	10315	10479	10703
0.51048	7266	7411	7508
0.25258	4120	4198	4323
0.10048	29	29	30
0.050184	− 3127	− 3174	− 3239
0.010021	−11518	−10662	−10864
0.005009	−13808	−14015	−14193
0.001001	−21471	−21797	−22193

From the free-energy decrease attending the cell reaction at the various concentrations we can now obtain, by subtraction, the free-energy decrease attending the transfer of one mole of potassium bromide from a solution of any given concentration to one exactly 0.1 *M*. These values expressed in joules are given in the accompanying table.

Measurement of Concentration Cells without Ion Transference.—

(**B**). Ag | AgBr, KBr (c_1) | $K.Hg_x - Hg_x.K$ | KBr (c_2), AgBr | Ag.

(**C**). $K.Hg_x$ | KBr (c_1), AgBr | Ag—Ag | AgBr, KBr (c_2) | $Hg_x.K$.

The particular construction of the cell used rendered easy and convenient the determination of the electromotive forces of cells of both types, (**B**) and (**C**). In every set-up a complete set of readings was made on each type of cell and the potentials compared. Since the electromotive force of either of these cells depends, at any given temperature, solely upon the logarithms of the ratios of the activity products of the two ions at the molal concentrations (c_1) and (c_2), the electromotive forces of (**B**) and (**C**) should be identical. The mean potentials of each of the two types do not in any case differ by more than 0.03 m.v. For this reason we have entered in Table IV only those potential readings derived from Cell **B**. These data are easily reproducible and are accurate to 0.03 m.v.

TABLE IV.

ELECTROMOTIVE FORCES OF CONCENTRATION CELLS WITHOUT ION TRANSFERENCE.

c_1.	c_2.	E_{25} volts.	E_{30} volts.	E_{35} volts.
2.8032	0.25258	0.11976	0.12194	0.12415
1.03486	0.10048	0.10672	0.10861	0.11049
0.51048	0.10048	0.07514	0.07643	0.07772
0.25258	0.10048	0.04263	0.04336	0.04408
0.51048	0.050184	0.10732	0.10914	0.11096
0.10048	0.010021	0.10892	0.11078	0.11268
0.050184	0.005009	0.11064	0.11251	0.11442
0.010021	0.001001	0.11346	0.11538	0.11732

The Free Energy of Dilution and the Decrease in Heat Content Attending the Transfer of One Mole of Potassium Bromide from Concentration c_1 to c_2.—The decrease in free energy, expressed in joules, attending the transfer of one mole of potassium bromide from concentration c_1 to concentration c_2 has been obtained by multiplying the electromotive force of the cell by 96494. These results together with the temperature coefficients of free energy decrease are given in Table V. The values for the decrease in heat content attending the same transfer have also been calculated and are included in the same table. The value of α, if potassium bromide behaved as a perfect solute, would be 0.003353. The corresponding decrease in heat content is zero. While these theoretical values are approached it will be observed that even at the highest dilutions employed potassium bromide does not behave as a perfect solute.

TABLE V.

THE FREE ENERGY OF DILUTION AND THE HEAT-CONTENT DECREASE ATTENDING THE TRANSFER OF ONE MOLE OF POTASSIUM BROMIDE FROM CONCENTRATION c_1 TO c_2.

c_1.	c_2.	$(-\Delta F)_{25}$ joules.	$(-\Delta F)_{30}$ joules.	$(-\Delta F)_{35}$ joules.	$\alpha\times10^6$.	$\beta\times10^6$.	$(-\Delta H)_{25}$ joules.
2.80320	0.25258	11556	11767	11980	+3617	+3.0	−896
1.03486	0.10048	10298	10480	10662	+3551	−1.8	−602
0.51048	0.050184	10356	10531	10707	+3382	+0.4	− 84
0.10048	0.010021	10510	10690	10873	+3380	+6.0	− 79
0.050184	0.005009	10676	10957	11041	+3365	+7.0	− 41
0.010021	0.001001	10947	11133	11320	+3360	+3.6	− 37

Measurements of the Cells with Ion Transference.—Ag | AgBr, KBr (c_1) | KBr (c_2), AgBr | Ag. The cells with ion-transference employed in this work were made by joining two of the half-cells containing silver bromide electrodes by a flowing-junction device similar to that described and used by Lamb and Larson.[13] This arrangement gave results that were easily reproducible to 0.03 m.v. Table VI contains a summary of these results.

TABLE VI.

ELECTROMOTIVE FORCES OF CELLS WITH ION TRANSFERENCE.

c_1.	c_2.	E_{25} volts.	E_{30} volts.	E_{35} volts.
2.8032	0.25258	0.05811	0.05928	0.06073
1.03486	0.10048	0.05237	0.05341	0.05443
0.51048	0.050184	0.05311	0.05406	0.05498
0.10048	0.010021	0.05394	0.05487	0.05587
0.05018	0.005009	0.05491	0.05582	0.05682
0.01002	0.001001	0.05627	0.05731	0.05834

The Transference Numbers of the Potassium Ion.—Thermodynamically the electromotive force of a concentration cell with ion transference is given by the relation:

$$E_t = \frac{N_K RT}{F} ln \frac{C_1^2.\alpha_1^+.\alpha_1^-}{C_2^2.\alpha_2^+.\alpha_2^-},$$

where N_K represents the transference number of the potassium ion, (α_1^+, α_1^-) and (α_2^+, α_2^-) are the activity coefficients of the ions at concentrations c_1 and c_2, respectively.

The corresponding expression for the electromotive force of a cell without ion-transference is

$$E = \frac{RT}{F} ln \frac{C_1^2.\alpha_1^+.\alpha_1^-}{C_2^2.\alpha_2^+.\alpha_2^-}.$$

The ratio, $\frac{Et}{E} = N_K$, gives us directly the transference number of the potassium ion. These values are recorded in Table VII. From these results it is to be observed that dilution is accompanied by a slight but

[13] Lamb and Larson, *J. Am. Chem. Soc.*, **42**, 229 (1920).

gradual increase in the transference number. The effect of temperature change is practically negligible between 25° and 35°.

TABLE VII.

TRANSFERENCE NUMBER OF THE POTASSIUM ION.

c_1.	c_2.	$(N_K)_{25}$	$(N_K)_{30}$	$(N_K)_{35}$
2.8032	0.25258	0.485	0.486	0.489
1.03486	0.10048	0.491	0.492	0.493
0.51048	0.050184	0.495	0.495	0.496
0.10048	0.010021	0.495	0.496	0.496
0.050184	0.005009	0.496	0.496	0.497
0.010021	0.001002	0.496	0.497	0.497

The Activity Coefficients of the Ions.—From the observed electromotive forces, Table IV, it is possible to calculate, by adding algebraically, the electromotive force of a cell containing any two of the concentrations employed in this work. In this manner the electromotie forces given in the following table have been computed. If now we make the assumption that at 0.001001 M (0.001 N), the activity of the ions is equal to their concentration, as determined from conductance measurements, the product of the activity coefficients, $\alpha_{K+}.\alpha_{Br-}$, at any other concentration can be calculated directly. These values, thus calculated, are given in Table VIII.

TABLE VIII.

THE ELECTROMOTIVE FORCES OF CONCENTRATION CELLS INVOLVING EACH CONCENTRATION (c) WITH 0.0010017 M AND THE ACTIVITY COEFFICIENT PRODUCTS AT THE CONCENTRATION (c).

c.	E_{25}	$(\alpha_{K+}.\alpha_{Br-})_{25}$
2.8032	0.38447	0.3625
1.03486	0.32910	0.3390
0.51048	0.29752	0.3945
0.25258	0.26501	0.4690
0.10048	0.22238	0.5510
0.050184	0.19020	0.6245
0.010021	0.11346	0.7914
0.005009	0.07956	0.8493
0.001001	0.00000	0.9565

In their study of the activity of largely ionized substances, Noyes and MacInnes[3] have computed from electromotive-force data the mean activity coefficients of the ions of potassium hydroxide, potassium chloride, lithium chloride and hydrochloric acid. Since for any given concentration the potassium and chloride ions are assumed to possess equal activities, the mean activity coefficients for this salt may be considered as the activity coefficient of either of its ions. If now we assume that at any given concentration the activity of the potassium ion is a constant and independent of the anion associated with it, we are in a position to calculate the activity of the bromide ion. In order to make these calculations the values of

$\alpha_{K+}.\alpha_{Br-}$, (Table VIII), were plotted on a large scale against the logarithms of the concentrations. From the curve thus obtained the values of $\alpha_{K+}\alpha_{Br-}$. corresponding to round concentrations were then read. These activity coefficient products were then divided by the value of α_{K+} for potassium chloride at the same concentration, taken from the data of Noyes and MacInnes.[3] The quotients obtained are obviously the activity coefficients of the bromide ion.

The results of these computations are summarized in Table IX. The second column contains the values of $\alpha_{K+} = \alpha_{Cl-}$ taken from the data of Noyes and MacInnes. Col. 3 contains the values of $\alpha_{K+}.\alpha_{Br-}$ read from the curve, while Col. 4 contains the values of α_{Br-} calculated in the manner described in the preceding paragraph. The values given in the fifth column are the values of α_{Br-} calculated in a similar manner from the data of Lewis and Storch.[14]

TABLE IX.

THE ACTIVITY COEFFICIENTS OF THE IONS AT ROUND CONCENTRATIONS.

c	$\alpha_{K+} = \alpha_{Cl-}$	$\alpha_{K+}\alpha_{Br-}$	α_{Br-}	α_{Br-}
2.800	.....	0.3625	0.602	.....
1.000	0.593	0.3440	0.579	.....
0.700	0.618	0.3788	0.613	.....
0.500	0.638	0.4045	0.634	.....
0.300	0.673	0.4525	0.672	.....
0.100	0.745	0.5540	0.743	0.742
0.050	0.790	0.6260	0.792	.....
0.030	0.823	0.6785	0.824	0.822
0 010	0.890	0.7930	0.891	0.886
0.005	0.923	0.8520	0.922	.....
0.003	0.943	0.8885	0.942	.....
0.001	0.979	0.9565	0.978	.....

A glance at the above table shows conclusively that at equal molal concentrations, at least up to 0.5 M, the activity coefficients of the chloride and bromide ions are identical. Furthermore, the close agreement between the values of the activity coefficients of the bromide ion computed from the data for potassium bromide and those calculated from the data for hydrogen bromide is further evidence of the independent activity of the individual ions.

Since the completion of the experimental part of this paper there has appeared an article by Lewis and Randall[15] on the activity coefficients of strong electrolytes. Using the data of Bates and Kirschmann[16] on the partial vapor pressures of the hydrogen halides, Lewis and Randall have arrived at the same conclusion regarding the activity coefficients of the

[14] Lewis and Storch, *J. Am. Chem. Soc.*, **39**, 1544 (1917).

[15] Lewis and Randall, *ibid.*, **43**, 1112 (1921).

[16] Bates and Kirschmann, *ibid.*, **41**, 1991 (1919).

chloride, bromide and iodide ions. These results indicate further that the differences observed in the activity of the various uni-univalent halides, when at the same concentration, are due primarily to differences in the activity of the cations.

Summary.

1. Measurements of the electromotive forces of the cells

$$Ag \mid AgBr, KBr\ (c) \mid K.Hg_x$$

have been made.

2. The free-energy decrease and the decrease in heat content attending the reaction in these cells have been calculated.

3. The free energy decrease attending the transfer of one mole of potassium bromide from various concentrations (c) to 0.10 M have been computed.

4. The electromotive forces of concentration cells with ion transference and without ion transference have been measured. From these values the transference numbers of the potassium ion have been calculated.

5. The free-energy decrease and the heat-content decrease accompanying the transfer of one mole of potassium bromide from concentration c_1 to concentration c_2 have been computed.

6. The activity coefficients of the bromide ion have been calculated and a comparison made of the activity coefficients of the chloride and bromide ions. For all concentrations up to 0.5 M the activity coefficients of these two ions are practically equal.

BIOGRAPHY

Harry Bryant Hart received his early education in the schools of Dexter, Kansas. In 1912 he entered the Kansas State Normal College and graduated in 1916 with the degree of Bachelor of Science.

He entered the State University of Iowa in 1918 where he pursued graduate work in Chemistry. In 1919 he received the Master of Science degree from this institution. For the year 1920–21 he was appointed to a Fellowship by the Graduate College. He is a charter member of the Iowa chapter of Gamma Alpha the national graduate scientific fraternity.

He is now employed as a research chemist by the Eagle-Picher Lead Company, Joplin, Missouri.